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Poly(lactic acid) green composites using oilseed coproducts as fillers☆

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Abstract

Poly(lactic acid), PLA, is a biodegradable polymer made from renewable resources with similar mechanical properties to polypropylene. PLA is more expensive than petroleum-based plastics, and the use of low-cost fillers as extenders is desirable. Agricultural coproducts of the alternative oilseed crops, cuphea (C), lesquerella (L) and milkweed (M), were collected after the oil was recovered. PLA and various levels of coproduct (0–45%, w/w) were compounded by twin-screw extrusion and injection molded. As coproduct content increased, tensile strength for all PLA composites decreased consistent with the Nicolais–Narkis model. PLA-C exhibited increased stiffness. In contrast, the modulus of PLA-M and PLA-L decreased slightly. Unexpectedly, PLA-M showed extensive stress-cracking under tensile stress and exhibited an elongation value 50–200% greater than the PLA control. Acoustic emission showed ductile behavior of the PLA-M composite.
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Keywords: Green composites; Poly(lactic acid); Biobased polymers; Alternate oilseed crops

1. Introduction

Green composites use agricultural-based polymers and biodegradable plant-based fillers (Netravali and Chabba, 2003). Current polymer composites use materials derived from petroleum that are nonrenewable and nondegradable. Most polymer composites are difficult to recycle or incur substantial cost for disposal. Green composites can be used in nondurable applications, short term products, or indoor applications. Poly(lactic acid), PLA, is a hydrophobic polymer prepared from renewable

☆ Names are necessary to report factually on available data, however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval to the exclusion of others that may also be suitable.

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agriculture-based feed stocks which are fermented to lactic acid and then polymerized. PLA is biodegradable in soil, compost or water, and the degradation products of PLA are nontoxic to the environment. PLA has mechanical properties comparable to petroleum-based plastics and can be extruded and injection molded, but is currently more expensive (Garlotta, 2001). The use of renewable and biodegradable fillers is desirable to provide cost-competitive polymer composites. PLA has been blended with reinforcing fibers (Wollerdorfer and Bader, 1998; Oksman et al., 2003), polymers including starch (Wang et al., 1998; Martin and Averous, 2001; Gattin et al., 2002; Chen et al., 2003; Garlotta et al., 2003; Cao et al., 2003), and inorganic fillers (Bleach et al., 2002; Kasuga et al., 2003). In recent work, sugar beet pulp, a coproduct of sugar refining, was blended with PLA (Finkenstadt et al., 2006; Liu et al., in press).

Approximately 660 million metric tonnes of oilseed crops were harvested in the world in 2005, corresponding to approximately 120 million metric tonnes of plant oil.[1] Alternate oilseed crops can be used to replace imported vegetable oils and provide sources of raw materials needed to make biofuels reducing our dependence on petroleum imports and providing renewable energy sources. Being commercially produced in the United States (Minnesota and North Dakota), Cuphea is native to the tropics and subtropics of the Americas and produce oil rich in saturated medium chain fatty acids such as capric acid. Medium chain fatty acids are used in soaps, detergents, cosmetics, lubricants and food (Cermak et al., 2005). Lesquerella, a native U.S. plant, is currently being developed for commercial industrial applications in Arizona and Texas. It produces seed containing a hydroxy vegetable oil. The seed contains around 30% protein and 25–30% oil, of which 55–60% is lesquerolic acid, a hydroxy fatty acid (HFA) analogous to ricinoleic acid from castor oil. HFAs are important industrial feedstocks, normally imported castor oil, and are used in lithium greases, coatings, food grade lubricants, polyurethanes and cosmetics. Milkweed is a new industrial crop whose fiber (floss) is in the market as a component of hypoallergenic pillows and comforters. Its seed oil contains linoleic and oleic acids (Harry-O'kuru et al., 2002; Holser, 2003).

Industrial oils obtained from alternate oilseed crops are valuable to the United States because they may replace imported oils such as castor, palm kernel and coconut oils. Currently, cuphea, lesquerella, and milkweed are experimental crops grown on limited acreage although there is industrial interest to cultivate them as commercial crops. In order to improve the economic success of alternate oilseed crops, an effort was made to use the biomass coproducts in value-added products such as biodegradable composite materials.

2. Experimental

2.1. Materials

Poly(lactic acid), provided by Dow Cargill (Minneapolis, MN), contained over 90% L-lactide. The weight average molecular weight was 150,000. The glass transition (T_g) and melting temperature (T_m), determined by DSC, were 61 and 151 °C, respectively. Cuphea seeds (PSR23, *Cuphea viscosissima* × *C. lanceolata*) were provided by the USDA-ARS in 2004. Lesquerella seeds (*Lesquerella fenderli*) were provided by the U.S. Water Conservation Laboratory (USDA-ARS, Phoenix, AZ). Milkweed seeds were provided by the Natural Fiber Corporation (Ogallala, NE) and contained common milkweed (*Asclepias syriaca*) and showy milkweed (*A. speciosa*) seeds harvested from cultivated plots and natural stands. Oil was removed by pressing the oilseeds with a pilot scale expeller (Model L250, Heavy Duty Laboratory Screw Press, French Oil Mill Machinery Company, Piqua, OH). Cuphea, lesquerella, and milkweed press seed cake retained approximately 8%, 7%, and 10% residual oil, respectively. The protein content of the pressed seed cake was 20%, 31% and 47%, respectively. The moisture content was 5%, 9% and 10%, respectively. The pressed seed cake was ground and passed through a 300 μm screen.

2.2. Processing

Compounding was performed using a Werner-Pfleiderer ZSK30 co-rotating twin-screw extruder (Coperion Corporation, Ramsey, NJ). The barrel was comprised of 14 sections, giving a length/diameter ratio of 44:1. The screw configuration was reported earlier (Finkenstadt et al., 2006). The screw speed was 130 rpm. PLA was fed into barrel Section 1 using a gravimetric feeder (Model 3000, AccuRate Inc, Whitewater, WI). After melting the PLA, oilseed fiber was fed into barrel Section 7 using a loss-in-weight feeder. In all cases, the total feed rate was approximately 75 g/min. The barrel was heated using eight heating zones. The temperature profile was 135 °C (zone 1), 190 °C (zone 2) and 177 °C (zones 3–8). A die plate with two holes (4 mm diameter) was used. The melt temperature of the exudate at the die

[1] Food and Agriculture Organization of the United Nations, 2006, http://faostat.fao.org.

was approximately 160 °C. Residence time was approximately 2.5 min. Die pressure and torque were allowed to stabilize between formulations before sample was collected. Strands were pelletized using a Laboratory (2 in.) Pelletizer (Killion Extruders, Inc., Cedar Grove, NJ).

An ACT75B injection molder (Cincinnati Milacron, Batavia, OH) was used to produce ASTM D638-99 Type I tensile bars (Master Precision Mold, Greenville, MI) as described in previous work (Finkenstadt et al., 2006). Barrel temperature profiles were adjusted by cooling the feed section to facilitate injection molding. The cooling time was increased as the samples with high weight fractions of oilseed fiber did not mold as well as 100% PLA.

2.3. Characterization

Tensile properties of PLA–oilseed composites were evaluated using a mechanical property testing machine (Model 1122, Instron Corporation, Norwood, MA). The thickness of the individual tensile bars was measured before testing. The gauge length was 40 mm, and the strain rate was 50 mm/min. Mechanical properties included tensile strength and modulus. Tensile strength is the maximum stress a sample can sustain without fracture. Modulus describes the stiffness of the material and is determined from the slope of the line tangent to the stress–strain curve. All samples were conditioned for at least 48 h at standard room temperature and humidity (23 °C and 50% RH).

Acoustic emission (AE) was used to probe the deformation of the green composites caused by an external force. Composite deformation (as the composite sample is squeezed, torn or stretched) is accompanied by a rapid movement, relocation, or breaking of structural elements such as fillers, fibers, matrices, and their interfacial areas. As a result, sound waves are produced that can be detected by an acoustic transducer and converted into electronic signals. This basic phenomenon is defined as an acoustic emission event and is translated by an AE analyzer as a “hit”. AE measurements were performed simultaneously during tensile stress–strain tests for all sample specimens. A small piezoelectric transducer was clipped against the sample specimen. This transducer (Model R15, Physical Acoustics Corp., Princeton Junction, NJ) resonates at 150 KHz, is 10 mm in diameter, weighs 20 g, and is coated with a very thin film of petroleum grease for more efficient acoustic coupling. AE signals emanating from this transducer during tensile measurements were processed with a Model 1220A preamplifier and a LOCAN-AT acoustic emission analyzer (Physical Acoustics Corporation, Princeton Junction, NJ). AE characterization was carried out on specimens using an upgraded Instron mechanical property tester (Model 1122 Instron Corp., Norwood, MA) with a gauge length of 102 mm and strain rate at 50 mm/min. Tests for each sample were performed five times to obtain an average value.

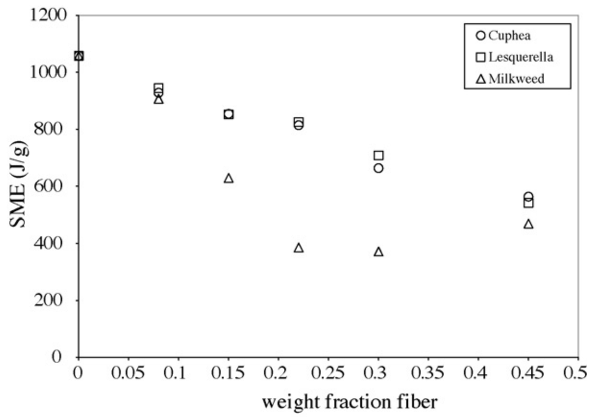

Fig. 1. Specific mechanical energy during extrusion of PLA–oilseed composites.

A dual-cell differential scanning calorimeter (Perkin-Elmer DSC 7, Newark, CT) with Pyris Series software was used to determine the thermal transitions of PLA and PLA–oilseed composites. Sample size was approximately 20 mg. The scan range was 20–180 °C with a rate of 10 °C/min.

Scanning electron microscopy of PLA-M fractured surfaces was conducted on a JEOL 6400 V scanning electron microscope (Peabody, MA).

3. Results and discussion

3.1. Processing

Specific mechanical energy (SME) was determined from torque and angular velocity measurements during extrusion. The net mechanical energy input to the screws was divided by the extrudate flow rate. SME for the PLA–oilseed composites is shown in Fig. 1. The total feed rate ranged from 73 to 83 g/min. SME for 100% PLA was 1058 J/g. For PLA-C and PLA-L, SME decreased gradually as the weight fraction of fiber increased. The reduction in SME is typical upon reduction of PLA feed rate when compounding a polymer with moisture containing fillers. The residual moisture of the PLA–oilseed composites after both extrusion and injection molding was approximately 1% (w/w). At 45% fill, SME was around 550 J/g. Earlier work using sugar beet pulp showed similar reductions in SME although at 45%

Table 1
Thermal properties of PLA–oilseed green composites

Weight fraction	Glass transition T_g (°C)	Heat capacity ΔC_p (J/g)	Crystallization temperature T_c (°C)	T_c onset (°C)	Melting temperature T_m (°C)	Enthalpy ΔH (J/g)	T_m onset (°C)	Dual peak T_m (°C)
Cuphea								
0.00	58.27	0.54	NA	NA	155.37	1.42	149.12	NA
0.08	56.17	0.47	NA	NA	155.70	6.26	148.18	NA
0.15	54.73	0.46	115.03	103.63	152.87	29.79	143.71	156.20
0.25	54.19	0.47	113.53	102.29	154.70	29.52	142.55	151.00
0.32	52.08	0.39	112.03	100.36	149.87	27.61	141.37	155.00
0.46	52.92	0.33	111.37	100.15	148.20	20.36	142.73	155.53
Lesquerella								
0.00	58.10	0.56	NA	NA	155.37	1.44	149.09	NA
0.07	56.78	0.50	NA	NA	155.70	1.41	148.73	NA
0.15	57.22	0.53	NA	NA	155.53	4.42	146.25	NA
0.19	56.02	0.48	119.53	106.92	154.53	25.35	146.17	NA
0.32	53.20	0.41	116.53	102.01	153.70	23.59	142.70	NA
0.45	51.14	0.30	113.37	99.34	148.70	17.98	141.72	154.70
Milkweed								
0.00	58.27	0.54	NA	NA	155.37	1.39	149.13	NA
0.07	54.46	0.46	126.03	106.59	154.03	19.42	145.34	NA
0.15	56.51	0.51	127.20	107.59	155.03	19.35	146.53	NA
0.20	56.48	0.43	127.87	109.44	155.03	16.63	146.55	NA
0.29	56.50	0.40	126.87	108.80	154.87	16.85	146.04	NA
0.45	57.04	0.30	124.53	108.94	154.87	16.72	145.58	NA

filler, the SME was around 700 J/g (Finkenstadt et al., 2006). The greater reduction in SME using oilseed crops can be attributed to the residual oil in the system which lubricates the polymer melt. For PLA-M, however, the decrease in SME was more pronounced for 15–30% fill. Examination of milkweed pressed seedcake revealed a waxy substance, which may have acted as a processing aid (Mpanza and Luyt, 2006). The presence of wax in the milkweed coproduct should also have an effect on the tensile properties of the PLA composites.

3.2. Thermal properties

After extrusion and injection molding, PLA control samples had a glass transition temperature (T_g) of

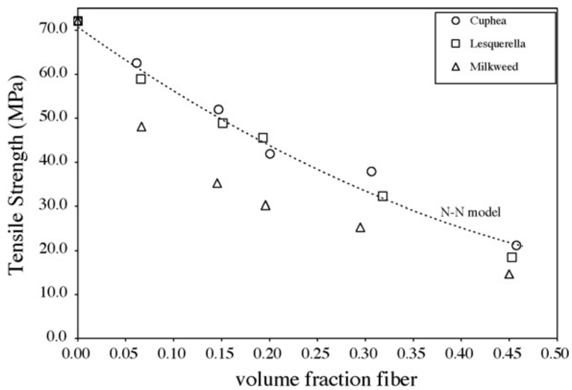

Fig. 2. Tensile strength of PLA–oilseed composites with Nicolais–Narkis model shown with dotted line.

Table 2
Mechanical properties of PLA–oilseed composites

Weight fraction	Tensile strength (MPa)			Young's modulus (MPa)			Elongation (%)		
	Cuphea	Lesquerella	Milkweed	Cuphea	Lesquerella	Milkweed	Cuphea	Lesquerella	Milkweed
0.00		72.2 (3.3)			1243 (94)			14.5 (3.8)	
0.08	62.6 (3.3)	58.9 (0.5)	48.1 (1.0)	1433 (38)	1386 (35)	1506 (66)	7.8 (0.8)	8.8 (0.9)	20.1 (6.4)
0.15	51.4 (1.3)	48.9 (0.8)	35.2 (0.4)	1433 (37)	1442 (42)	1397 (92)	6.1 (0.2)	7.6 (0.6)	34.6 (9.9)
0.22	41.9 (3.5)	45.6 (0.7)	30.3 (0.7)	1477 (60)	1350 (61)	1279 (62)	5.4 (0.8)	8.1 (1.0)	30.4 (4.5)
0.30	37.9 (0.4)	32.2 (0.8)	25.3 (0.6)	1540 (37)	1349 (170)	1240 (38)	7.9 (2.2)	10.7 (1.2)	23.1 (4.3)
0.45	21.2 (0.7)	18.5 (0.5)	14.7 (0.6)	1509 (66)	1239 (57)	967 (47)	4.6 (1.3)	11.0 (1.5)	14.3 (2.9)

The values in parentheses indicate standard deviations.

58 °C (ΔC_p = 0.55 J/g) and a melting temperature (T_m) of 155 °C (ΔH = 1.4 J/g). The onset of melting occurred around 149 °C. The addition of oilseed coproduct lowers the T_g, T_m and onset temperature for cuphea and lesquerella and is reflected in concurrent decrease of ΔC_p and increase in enthalpy, ΔH (Table 1). PLA–milkweed, however, shows no significant change in T_g or T_m as the amount of filler increases. A recrystallization peak (T_c) at 115 °C appears for cuphea (15% fill), at 119 °C for lesquerella (19% fill) and at 126 °C for milkweed (7% fill). A sharp increase of the enthalpy of the composites occurs at the same time as the PLA phase crystallizes. Low

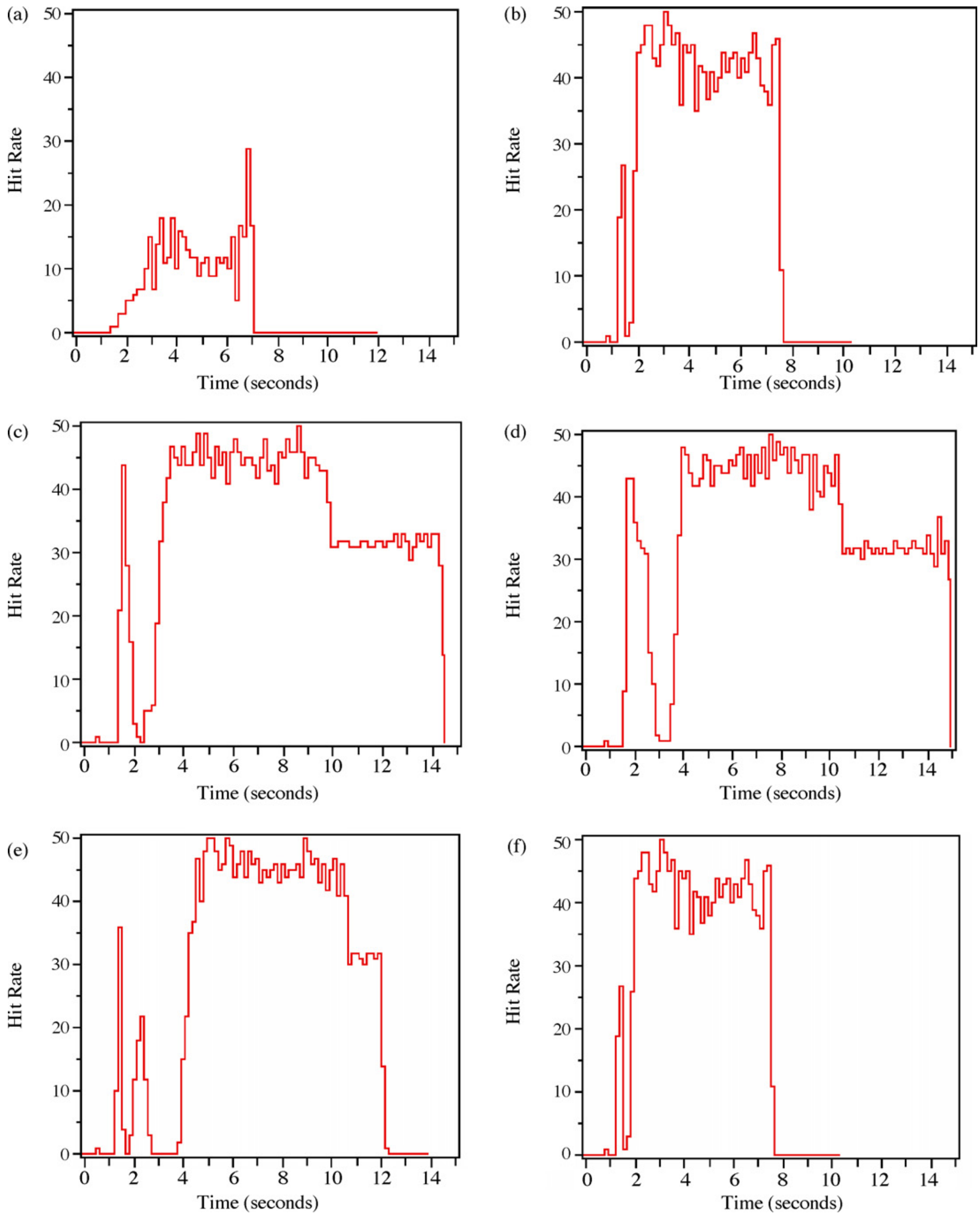

Fig. 3. Acoustic emission of PLA-M composites at (a) 100% PLA, (b) 8% milkweed, (c) 15% milkweed, (d) 22% milkweed, (e) 30% milkweed and (f) 45% milkweed.

values of enthalpy indicate that the PLA is amorphous; higher values of enthalpy indicate recrystallization of the PLA as the surface area of the matrix–filler interface increased with increases in the amount of filler. Clearly, the type of filler affects the thermal properties of the PLA green composites.

3.3. Mechanical properties

Tensile strength of the PLA composites decreased with the incorporation of oilseed coproduct (Fig. 2), consistent with the Nicolais–Narkis model for incorporation of a rigid, spherical filler calculated by $\sigma = \sigma_o[1 - 1.21(V_f^{2/3})]$ where V_f is the volume fraction of the oilseed coproduct used as filler and σ_o is the tensile strength of the PLA control (Nicolais and Narkis, 1971). Cuphea retained slightly more tensile strength than lesquerella indicating a stronger adhesion to the PLA matrix. Milkweed produced the weakest material below that predicted for nonadhesion of filler to PLA matrix; however, its modulus decreased significantly indicating a plasticizing effect not evident for PLA blended with cuphea and lesquerella (Table 2). The most significant effect is on the elongation of the PLA composites. Incorporation of cuphea and lesquerella showed no significant difference in elongation; however, milkweed showed a drastic increase in elongation with 8% filler although this value decreased with increasing amounts of filler. During testing, the PLA–milkweed composite showed stress-whitening that is attributed to the formation of voids in the material as the polymer deforms and stretches. The yielding phenomenon is not as pronounced in PLA composites with cuphea or lesquerella nor sugar beet pulp (Finkenstadt et al., 2006), and there was no ductile behavior exhibited (data not shown). After 21 days of aging in 50% RH and 20 °C, there was essentially no change in the tensile properties of the PLA–oilseed composites except for PLA–milkweed which had approximately a 10% reduction in modulus which indicates softening in the composite.

Acoustic emission (AE) analysis was performed during fracture testing of the PLA–milkweed composite. AE is plotted by recording the number of acoustic “hits” as a function of time. AE clearly shows ductile behavior of the composite. The 100% PLA sample produced a lower hit rate and cumulative hits than the samples with milkweed (Fig. 3a). Presumably this is due to its homogenous nature of a single component. Moreover, 8% milkweed samples showed a distinctive peak at 1–2 s before the main peaks appeared (Fig. 3b). This may indicate a separation or destruction of the interface between milkweed particles and PLA. This distinctive peak was also present for higher levels of filler. The most interesting result is that for 15–30% filler (Fig. 3c–e) where AE plots indicated ductile behavior occurred before the fracture point. There are clearly three phases in deformation as the PLA–milkweed composite is put under stress. The first phase is debonding of the filler from the PLA matrix (approx. 1–3 s under stress), the second phase is the yielding of the PLA matrix (approx. 4–10 s under stress), and the third phase is the ductile nature of the PLA (approx. 10–14 s under stress) probably due to the plasticization of PLA by the wax. At 45% milkweed, the ductile behavior is not present indicating that the defects in material integrity overwhelm any beneficial interaction between PLA and milkweed (Fig. 3f). Scanning electron micrographs of PLA-M fracture surfaces with 8% and 30% milkweed are shown in Fig. 4. The PLA fracture zones are clearly evident in Fig. 4a as are spots where the milkweed filler has pulled out of the PLA matrix corresponding with the AE plot in Fig. 3b. In Fig. 4b, the PLA fracture plates are softer and

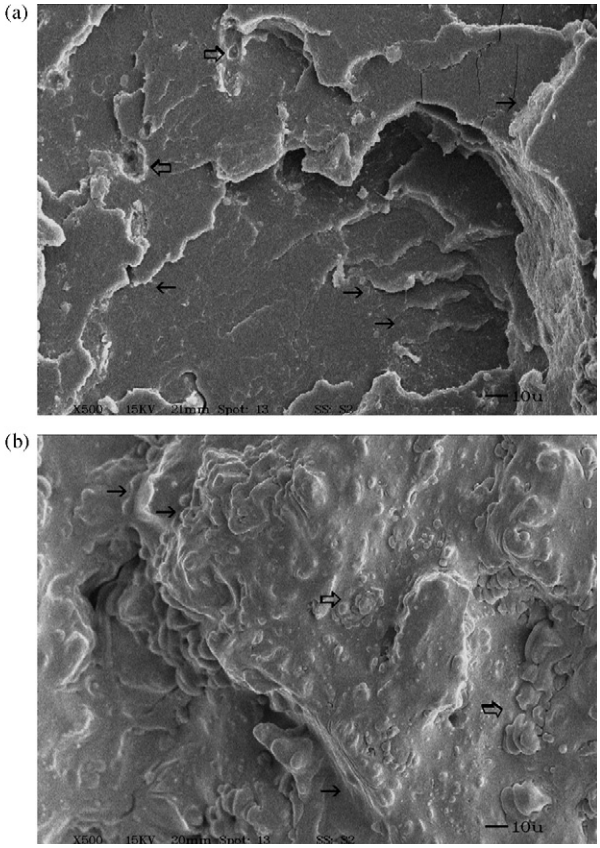

Fig. 4. SEM of PLA-M composites at (a) 8% fill and (b) 30% fill. PLA fracture plates are indicated with thin arrows. Open arrows indicate (a) filler pullout and (b) filler in the PLA matrix. Magnification is 500×. The scale bar is 10 μm.

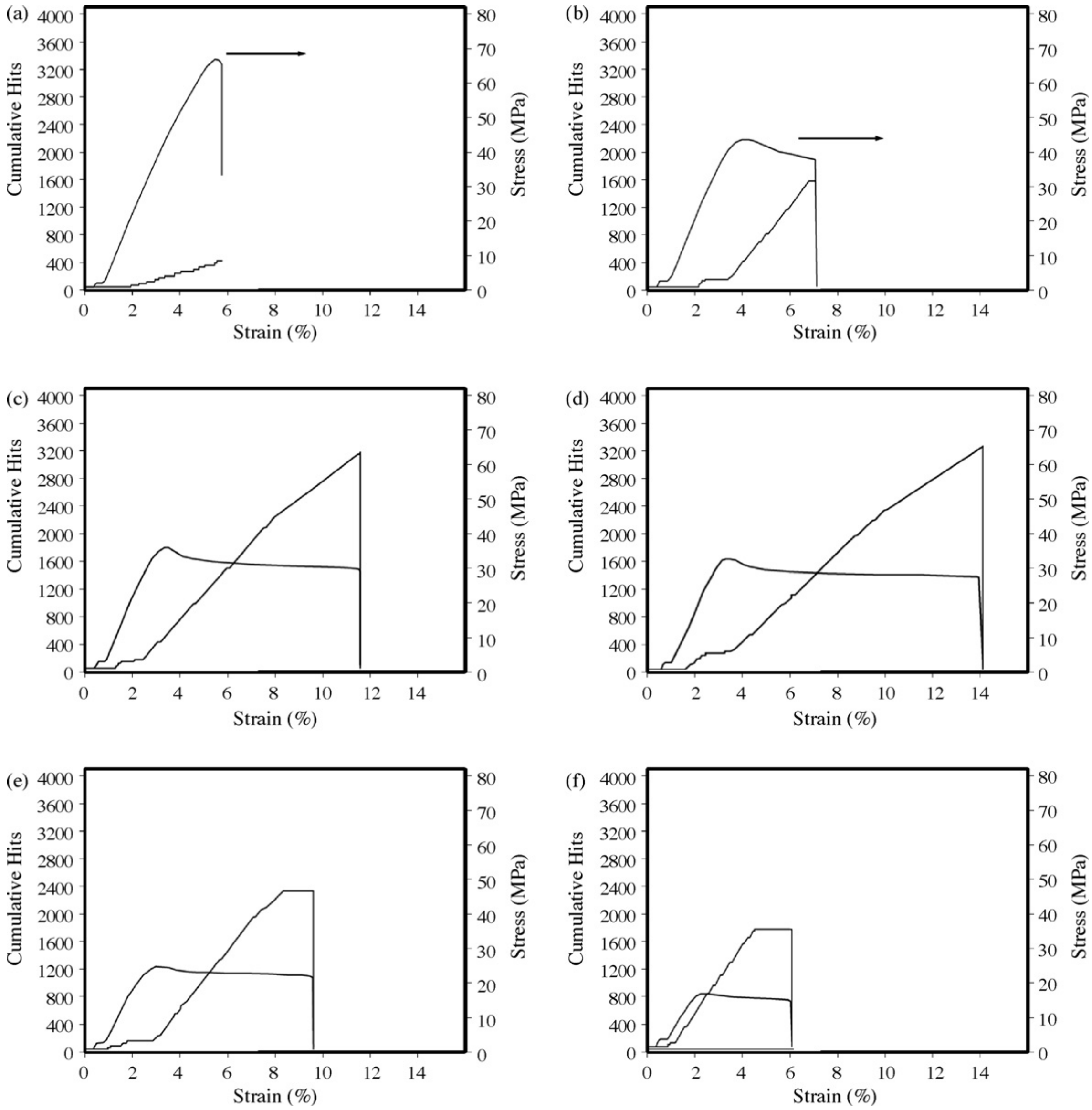

Fig. 5. Stress–strain curves and acoustic emission (cumulative hits) of PLA-M composites for (a) 100% PLA, (b) 8% milkweed, (c) 15% milkweed, (d) 22% milkweed, (e) 30% milkweed and (f) 45% milkweed.

less defined indicating a ductile behavior of the polymer with 30% milkweed as seen in the AE plot (Fig. 3e). Fig. 5 displays the relationship between the stress–strain curves and the corresponding acoustic emission signal (shown as cumulative hits). For 100% PLA, the acoustic emission signal increases as the strain increases until fracture at 72 MPa (Fig. 5a). As the milkweed content increases, the fracture strength decreases, and the PLA matrix exhibits yielding behavior which occurs quicker as the milkweed content increases. For PLA-M composites, the AE plot shows little noise (hits) until the modulus begins to increase as stress and strain increase simultaneously. AE begins to increase once the composite begins to yield (Fig. 5b–f). For 100% PLA, the composite fractured around 5% strain rate (Fig. 5a). As the milkweed content increased, the fracture point increased to a maximum of 14% strain for 22% milkweed (Fig. 5d). At 45% fill, the PLA matrix between particles is thin which translates to a much smaller energy consumption as the load-bearing area of the matrix is decreased (Fig. 5f). The filler–matrix debonding is strongly correlated in highly filled (45%) composites. Once debonding was initiated, the fracture plane occurred rapidly with little further elongation.

4. Conclusion

Oilseed coproducts can be used as low-cost fillers in PLA where the amount of filler may be adjusted to give the desired mechanical properties. Cuphea and lesquerella act as a particulate filler similar to sugar beet pulp while milkweed exhibits ductile behavior in PLA green composites.

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